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Organic solar cells: Their developments and potentials

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ABSTRACT

This paper aims to review the developments and the potentials of organic photovoltaic, which has caught the attention of researchers of optoelectronics. The paper briefly introduces the physics underlying organic photovoltaic devices of donor–acceptor interfaces. It examines a variety of materials and architectures that benefit the performance of the organic photovoltaic cell; along with the important photogeneration factors including the exciton diffusion length as well as charge transport, separation, and collection. The authors have reviewed the recent understanding of the mechanisms that govern these photocurrent generation steps and sketched out the search for alternative materials and device architectures. The review also discusses areas where active researches should be directed for cell efficiency improvement and outlines the issues to be resolved in order to speed up the commercialization.

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1. Introduction

The field of optoelectronics has seen important developments in the organic photovoltaic cells (OPVCs) and the light emitting diodes (LEDs) since 1990s. These two lines of work have a cross linked area, organic light emitting diodes (OLED) [1–3]. As the matured applications brought about by the maturing LED technology [4,5] is spreading, polymer photovoltaic is attracting general attention. The search for organic materials suitable for electronic applications dates back to the early 1950s. Polymer photovoltaic (or plastic solar cell) has been studied ever since. Kearns et al. [6] reported the photovoltaic effect of magnesium phthalocyanine (MgPh), a macrocyclic compound, as early as 1958. Since then, the topic has caught the attention of researchers and has been actively investigated due to the low-cost, light-weight, and elasticity of polymer materials [7,8].

The organic photovoltaic cells (OPVCs) are the form of polymer solar cells that produce electricity from sunlight using flexible polymers. Due to their higher band gaps, OPVCs have lower efficiencies when compared to inorganic photovoltaic cells.

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Table 1
Values of The integrated photon flux and maximum current density from direct and circumsolar (AM1.5D) as well as global (AM1.5G, ~1000 W/m^2) solar irradiation available for a photovoltaic that harvest light from 280 nm up to the wavelength, Assuming every photon converted into one electron in the external circuit.

Wavelength (nm)	Accumulated from 280 nm to the specified wavelength			
	Maximum harvested (%)		Current density (mA/cm^2)	
	AM1.5D	AM1.5G	AM1.5D	AM1.5G
500	8	9.4	5.1	6.5
550	12.5	14	8	9.7
600	17.3	19	11.1	13.2
650	22.4	24.3	14.3	16.8
700	27.6	29.6	17.6	20.4
750	32.6	34.7	20.8	23.9
800	37.3	39.5	23.8	27.2
900	46.7	48.8	29.8	33.7
1000	53	55	33.9	38
1100	61	62.9	39	43.4
1250	68.7	70.4	43.9	48.6
1500	75	76.5	47.9	52.8

Traditional crystalline inorganic semiconductors can absorb a continuous spectrum of light and has three-dimensional rigid lattice that provides great carrier mobility. A silicon solar cell with a band gap of 1.1 eV (a band gap wavelength of 1100 nm) can reach an AM1.5 power conversion efficiency of 22% [9]. While the best performing polymer solar cells are made with poly(3-hexylthiophene) (P3HT) as donor material. P3HT has a band gap of 1.9 eV (650 nm) and thus only has the possibility to harvest up to 22.4% of the available photons [10] and gives a maximum theoretical current density of 14.3 mA/cm^2 (see Table 1). Coupled with the most widely used acceptor material, [6,6]-phenyl-C61-butyric acid methyl ester (PCBM), The performance of a P3HT:PCBM system is nearing its optimal of about 5% [11–15], which is lower than a quarter of a silicon solar cell's optimal. Besides lower efficiencies, OPVCs' stability and strength are also lower compared to their inorganic counterpart as organics are more susceptible to oxygen and water.

Nevertheless, the low production costs of plastics combined with the flexibility of organic molecules marks the great potential of OPVCs for photovoltaic applications [16,17]. In addition, both the polymer photovoltaic device efficiency and the knowledge of the physical processes underlying OPVCs have improved significantly since the turn of the 21st century [18].

The efficiency of OPVCs has increased steadily to the current level of about 6%. Understanding and overcoming the loss mechanisms in processes from optical excitation to charge collection should lead to efficiencies of 10% in the near future [19]. In theory, power conversion efficiencies of around 15% should be possible with a single heterojunction. Stacking of multiple cells may be a key to higher efficiencies [20].

2. Photocurrent generation

Inorganic photovoltaic devices produce free charge carriers after the absorption of light. While in OPVCs an exciton (an electron–hole pair bound together by electrostatic) is generated after absorbing a photon. Fig. 1 is a schematic energy diagram of a D–A interface. Each material has a **highest occupied molecular orbital** (HOMO), or **ionization potential** (IP), and a **lowest unoccupied molecular orbital** (LUMO), or **electron affinity** (EA). A band gap is defined as the difference between energy levels of HOMO and LUMO in the polymer. The **open circuit voltage** (V_{oc}) is defined as the difference between the HOMO of the donor and the LUMO of the acceptor. The two layers of materials have differences in EA and IP, which set up electrostatic forces at the interface. When chosen properly, the differences can generate stronger electric fields that may break up the excitons more efficiently [21,22]. The exciton diffuses inside the material to reach the D–A interface and then separated into free holes and electrons by the electric field [23]. When reaching the D–A interface, the electron will be transferred to the material that possesses higher EA while the hole will be accepted by the material that has lower IP [24].

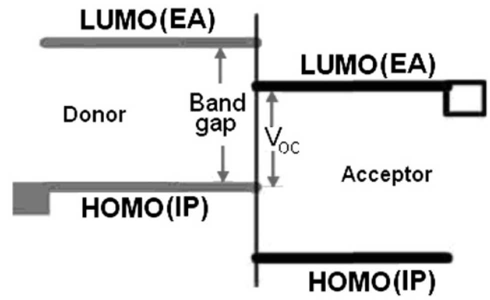


Fig. 1. A schematic energy diagram of a D–A interface. Each material has a HOMO (i.e., IP) and a LUMO (i.e., EA). The difference between the energy of HOMO and LUMO is the band gap. The difference between the HOMO of the donor and the LUMO of the acceptor is V_{oc}. The differences in EA and IP of the two materials set up electrostatic forces at the D–A interface.

The complete four-step photocurrent generation process starting from an absorbed photon and ending with charges collected at the electrodes is depicted in Fig. 2, where

a) the absorption of a photon results in an exciton,
b) the exciton diffuses towards the D–A interface,
c) the bound electron hole pair disassociates into free carriers, and
d) the free carriers transport towards the electrodes for collection.

Each of these steps has its corresponding loss mechanism, namely, non-absorbed photons in step a, exciton decay in step b, geminate recombination of the bound pair in step c, and bimolecular recombination in step d. The four phases are interrelated. Improving a single could but not necessarily lead to the overall or expected improvement.

There are different types of D–A interface structures. A simple bilayer (or planar, single) heterojunction is the simplest D–A interface architecture used for OPVCs. The simple bilayer cells are made via sandwiching two layers of organic electronic materials between two metallic conductors, typically a layer of indium tin oxide (ITO) with high work function and a layer of low work function metal such as Al, Mg, or Ca. The organic layer with higher EA and IP is the acceptor, and the other organic layer is the donor. The basic structure of such cell is illustrated in Fig. 3. A double heterojunction is the device that stacks two single heterojunctions (Fig. 4).

An interpenetrating group of donor and acceptor materials called bulk (or dispersed) heterojunction (BHJ, as illustrated Fig. 5) is introduced to reduce the average distance between donor and acceptor molecules without reducing the overall thickness of the device active layers [19,25]. In a BHJ, the donor and the acceptor are mixed to form a polymer blend with the distance scale between the donor and the acceptor similar to the exciton diffusion length. The excitons generated in either material may reach the D–A interface more readily for efficient disassociations. The electrons then move to the acceptor domains and are carried through the device to be collected by one electrode, while

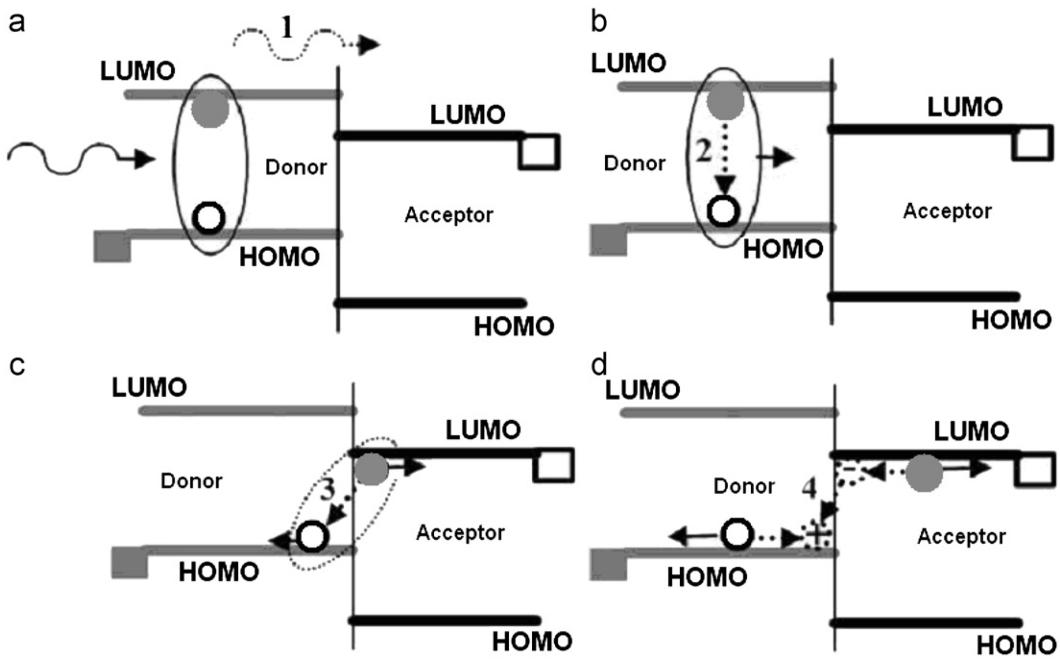


Fig. 2. The scheme of the operative sequence of an OPVC. The photocurrent generation process is depicted: (a) generation of excitons by photon absorption, (b) diffusion of excitons to the heterojunction, (c) dissociation of the excitons into free charge carriers, and (d) transport of the carriers to the electrodes for collection. Loss mechanisms are also indicated: (1) non-absorbed photons, (2) exciton decays, (3) geminate recombinations of the bound pair, and (4) bimolecular recombinations.

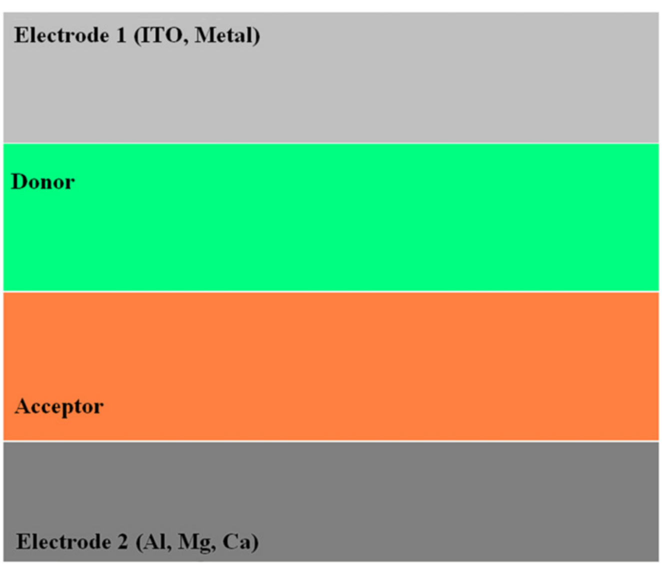


Fig. 3. The basic structure of a simple bilayer heterojunction. This planar heterojunction is made via sandwiching two layers of organic electronic materials between a metal layer of high work function and a metal layer of low work function.

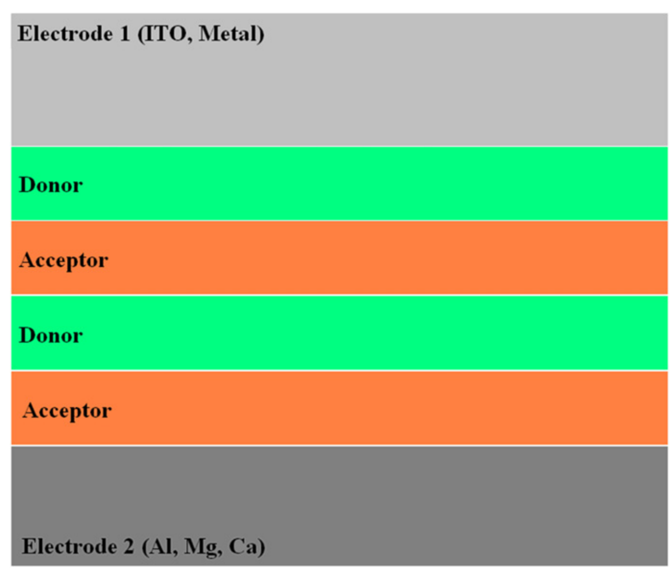


Fig. 4. The architecture of a double heterojunction device. The stacking of two single heterojunctions makes a double heterojunction. Stacking *n* single heterojunction leads to a multiple heterojunction.

the holes are pulled toward the opposite direction to be collected at the other side. BHJs have higher quantum efficiencies compared to the bilayer heterojunction, because in BHJ it is more likely for an exciton to find a D–A interface within its diffusion length.

2.1. Light absorption

The absorption efficiency of an OPVC is, to a great extent, determined by how closely the spectral response of the polymer matches with the solar spectrum. Low light absorption efficiency leads to low photocurrent production. As mentioned, the best performing polymer solar cells to date are made with P3HT, which has a band gap of 650 nm, and is only able to harvest up to 22.4% of the available photons. Such poor matching of P3HT's photon absorbance with the solar cell spectrum is its main disadvantage. This gives good reason for the research for new materials that have better aligned energy levels to harvest photons at the longer wavelengths.

One interesting approach to enhance light absorption is by narrowing the donor band gap. Lowering the band gap allows for

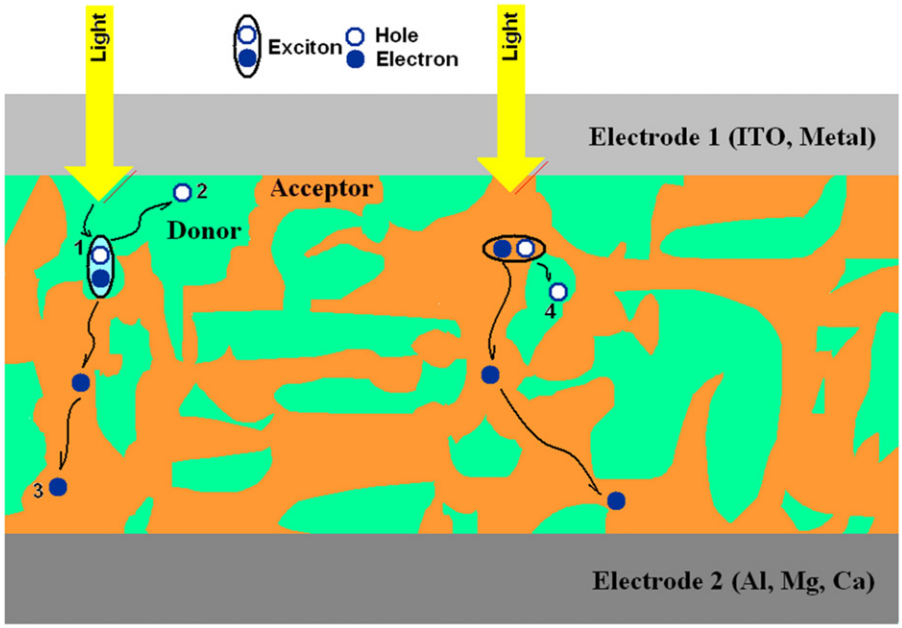


Fig. 5. The structure of a BHJ. This design greatly increases the interface area between the donor and the acceptor and leads to a better production of separated charges. As depicted in the diagram, (1) exciton created by incident light diffusing towards a D–A interface; (2) hole drifting towards electrode; (3) electron moving towards electrode; (4) hole trapped in an isolated island of organic molecule. Charge carriers can sometimes be trapped within the randomly separated materials and fail to reach the electrodes.

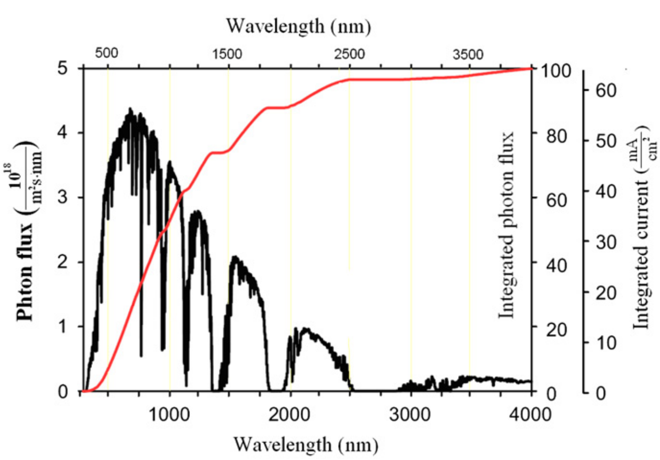


Fig. 6. Photon flux from the sun at AM1.5D illumination as a function of wavelength. The integral of the curve, which reflects the data from the AM1.5D column of current density section of Table 1, is shown as the percentage of the total number of photons and the obtainable current density on the right y-axis. The range of wavelengths from 280 nm to 400 nm amounts to only ~1.4% of the total possible current or ~1 mA/cm^2 in current density.

absorption of more photons, which results in higher currents that could lead to higher power conversion efficiency [26,27]. Thus, low band gap OPVC materials are needed in order to optimize photon harvesting [28]. A low band gap polymer is loosely defined as a polymer with a band gap below 2 eV, which absorbs light with wavelengths longer than 620 nm. Low band gap polymers have the possibility to improve the efficiency of OPVCs due to a better overlap with the solar spectrum. For example, when the band gap drops from 1.9 eV to 1.1 eV (that is, when the band gap wavelength increases from 650 nm to 1100 nm), photocurrent will gain considerably as the obtainable current density increases from 14.3 mA/cm^2 to 39 mA/cm^2 (Fig. 6).

Two models proposed by Scharber et al. [29] and Koster et al. [30] predict that a higher efficiency of OPVCs can be achieved using a lower band gap polymer. The V_{OC} defined in the two models is the difference between the HOMO of the donor and the LUMO of the acceptor. Combining the low band gap with a higher LUMO of the acceptor results in an increase of the V_{oc} and hence the efficiency is increased. The field of low band gap polymer materials for OPVCs is emerging. The current issue is how to synthesize large quantity of materials that are sufficiently pure for OPVCs. Whether or not the practically achievable efficiencies for low band gap materials may coincide with the theoretical value, it is important to extend absorption beyond 620 nm.

Some conjugated materials show elevated and wide-ranging spectrum absorption. Two conjugated polymers can be tuned to harvest a wider range of solar spectrum as the materials' molecular structures and aggregate tendency have a substantial influence on the absorption. Conjugated π-systems, often referred to as organic semiconductors, have been used as both donor and acceptor materials [31]. When arrive at an ordered solid crystalline structure, the organic semiconductors absorption band broadened and thus benefits the cell efficiency [32].

The proper use of a dye can improve the light absorption of the material. Ismail et al. [33] have studied the effect of 9,10-diphenylanthracene (DPA) on light harvesting and performance of solar cell composed from poly P3HT:PCBM blend films. The results indicate that by adding specific amounts of DPA into P3HT:PCBM blend, the light harvesting can be improved. The external quantum efficiency (EQE or QE, the short-circuit current to incident photon flux ratio) and cell performance parameters have also improved due to the charge carrier transfer taking place between P3HT and PCBM through the conjugated DPA molecules.

Kymakis and Amaratunga [34] have developed a molecular dispersed heterojunction solar cell that consists of a polymer and a dye coated carbon nanotubes blend. These materials are sandwiched between metal electrodes via incorporating a high absorbing organic dye at the polymer/nanotube junctions. Such device has increased the layer absorption dramatically and generated an I_{sc} 5 times greater than the non-dye system. Unfortunately, the power conversion efficiency is not governed by the current density alone. A high V_{oc} is also needed for power increase. Due to the lower energy of the charge carriers at longer

wavelengths the voltage difference that the device can produce is dropped. As the V_{oc} of such device has dropped 0.1 V, the overall cell performance has not improved significantly.

Koeppe et al. [35] have introduced the use of a luminescent collector for extending the absorption range of organic solar cells. Instead of generating charge directly, this collector absorbs light that would otherwise not be absorbed in the cell and then emits light within the absorption spectrum of the solar cell active layers. A 15% increase in short circuit current (I_{sc}) has been recorded after such implementation.

Certain architecture employed in small-molecular weight based solar cells can also improved absorption efficiency. For example, Rand et al. [36] have developed an architecture that incorporates low mobility materials into an efficient device structure. They have deposited an ultra thin SnPc molecular layer in between CuPc and C_{60} films. As the SnPc layer has a very high absorption coefficient which extends to 1000 nm, this development represents an important step toward achieving OPVCs with absorption in the near infrared segment.

Bailey-Salzman et al. [37] have demonstrated the use of chloroaluminum phthalocyanine (ClAlPc) as a donor and C_{60} as an acceptor in planar double heterojunction OPVCs and have also extended the spectral response of the device to the near infrared.

Paul et al. [19] have shown that non-planar phthalocynanines have appealing absorption characteristics, however, with a side effect that would reduce charge carrier transport. The donor layer has to stay ultra thin to counter the side effect. As a result, all layers of the device have to be tuned to account for optical interference. Molecules offering a compromise between absorption and carrier mobility should allow for improvements.

2.2. Exciton diffusion

The exciton diffusion length (L_D) is the parameter that governs whether or not the exciton can diffuse to the interface. The excitons with longer L_D have better chances to reach the D–A interface. The typical exciton diffusion lengths in polymeric materials are 1–10 nm [38,39]. Only the photons absorbed within this range of distances from the interface can contribute to the device current. Therefore, the number of excitons that can reach the interface and break up into carriers will maximize if the layer thickness is within the range of their diffusion lengths. Unfortunately, a polymer layer needs a thickness of at least 10 nm to absorb enough light. Only a fraction of the excitons can reach the D–A interface at such a thickness. As a result, the efficiencies of the simple bilayer structures are cut short because their D–A interfaces are beyond the reaching range of some excitons [40].

Finding a mechanism that would increase the exciton L_D is a way to deal with exciton diffusion issue. Paul et al. [9] have propose a method for increasing the exciton diffusion length by converting singlet excitons into long-lived triplets. By doping a polymer with a phosphorescent molecule, they have demonstrated an increase in the exciton L_D of a polymer from 4 to 9 nm. Peumans et al. [41] have used materials with extended exciton L_D to fabricate highly efficient double heterojunction photovoltaic cells. These researchers have used C_{60} as an acceptor material to obtain double heterostructure external power conversion efficiencies of 3.6% ± 0.4% under 1 sun AM1.5 illumination, even without a light trapping geometry.

Most researchers focus on decreasing the distance between donor and acceptor instead of searching for new molecules to increase diffusion lengths [21,42–44]. For example, Peumans et al. [38] have found that, for single heterojunction cells, the need for direct contact between the deposited electrode and the active organics leads to quenching of excitons. An improved device architecture, the stacking of two single heterojunctions (which is a double heterojunction devices), is shown to confine excitons within the active layers, allowing significantly higher internal efficiencies. Thin bilayer OPVC can be stacked with ultrathin (~5 Å), discontinuous Ag layers between adjacent cells serving as recombination sites for electrons and holes generated in the neighboring cells. Stacking of n (the number of cells in the stack) single heterojunction devices leads to thin film multiple heterojunction OPVCs. Such stacked cells have V_{oc} that are n times of that of a single cell. In optimized structures, the I_{sc} remains approximately constant upon stacking thin cells, leading to higher achievable power conversion efficiencies. An OPVC with 2.4% ± 0.3% power efficiency under AM1.5 illumination conditions

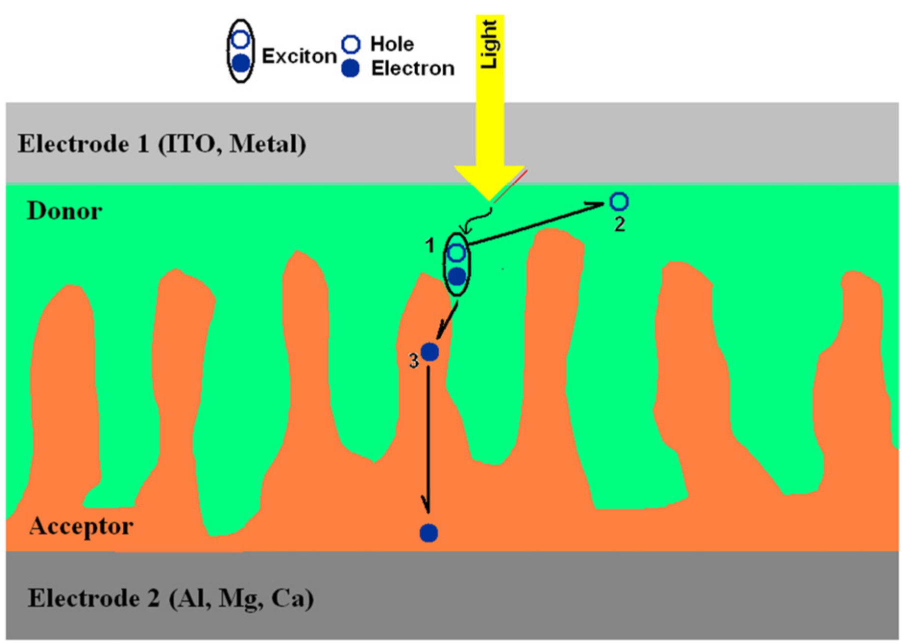


Fig. 7. The structure of an OHJ, a heterojunction with controlled growth. OHJs provide better control over the donor–accept materials positioning and has better QE than that of highly disoriented heterojunctions. As depicted: 1. Incident light creating exciton, 2. hole traveling towards electrode, 3. electron moving towards electrode. Charge carriers do not get trapped within the orderly separated materials.

is obtained by stacking two 1% ± 0.1 efficient devices. On the other hand, the elimination of the contact layers between the stacked cells puts together a multilayer structure consisting of alternating films of donor and acceptor-type materials. As the ~5 Å individual layers can be substantially smaller than the exciton diffusion length, nearly 100% of the photo-generated excitons are dissociated with the resulting free charges detected. In addition, the ultrathin organic layers facilitate electron and hole transport through the multilayer stack by tunneling. Combining the double heterostructure with novel light trapping schemes, devices with external efficiencies approaching their internal efficiency are obtained.

Another way to deal with the issue of insufficient diffusion length is to acquire a structure (such as BHJ) that can adopt short diffusion lengths.

After the dissociation of the exciton, the resulting electron and hole may still be joined as a geminate pair. An electric field is required in order to separate them. Once separated, the electron and hole must be collected at contacts. The random oriented domains of donor and acceptor in a BHJ (as shown in Fig. 5) tends to deteriorate the system conductivity and thus the cell efficiency. Paul et al. [19] have demonstrated that non-planar phthalocynanines have appealing absorption characteristics but also have reduced charge carrier transport. By using ultrathin donor layer and tuning all the device layers to justify optical interference effects, these researchers have come up with cells of 3.1% efficiency for the non-planar chloroboron subphthalocyanine donor. Molecules offering a better compromise between absorption and carrier mobility should allow for further enhancements.

Heterojunction with controlled growth can reach a structure called the ordered heterojunctions (OHJ, see Fig. 7). OHJs provide better control over the D–A materials positioning, which results in better QE than that of highly disoriented heterojunctions, and therefore may be the next logical step beyond BHJs. OHJs are usually fabricated with ordered inorganic materials and organic active regions. These types of heterojunctions have a more restrictive thickness limitation as the carriers have to diffuse to a contact along the length of the pore through the polymer. In an ideal OHJ, all absorbed photons will be in the vicinity of a D–A interface and can contribute to photocurrent generation [45,46]. Enhancing the carrier mobility, with a major challenge in controlling morphology inside the confines of the pores, will be the answer to further performance improvement of OHJ devices.

2.3. Charge dissociation and transport

Charge collection requires dissociation of excitons at the D–A interface. The differences in EA and IP between donor and acceptor layers set up electrostatic forces at the interface. When chosen properly, the electric fields generated from such differences can break up the excitons into electrons and holes efficiently. The electrons are then accepted by the material with higher EA and the hole by the material with lower IP. Unfortunately, as a charge travels to the electrode, it can recombine or become trapped in a disordered interpenetrating organic material and thus causes efficiency drop.

Film morphology can also have a drastic effect on the QE of the device. A good morphology (i.e., a smooth film) would increases QE and as a result the performance of the device. Rough surfaces and presence of voids can increase the chance of short circuiting. They also raise the series resistance and thus reduce the current output. While the BHJ structures is designed to reduce distances between excitons and D–A interfaces, the amorphous and disordered structures of some BHJ tend to lead to charge recombination (Fig. 5). As mentioned, an OHJ (Fig. 8) provides better control over positioning the D–A materials and thus results in better power efficiency than that of highly disoriented heterojunctions. Therefore, choosing suitable processing parameters to better control the structure and film morphology is desirable [47].

Peumans et al. [48] have demonstrated that film morphology can be improved by annealing of a device after covering it by ~1000 Å thick metal cathode. The metal cap on top of the organic film applies stresses on the organic film and confines the organic materials during annealing. This procedure prevents the formation of a rough surface morphology while allowing for the formation of an interpenetrating D–A interface inside the bulk of organic thin film.

Various research groups have employed different solvents for spin coating the active layer and have shown that the evaporation time of the solvent has significant influence on the morphology of the active layer [49]. However, a real control on the morphology of these systems has yet not been achieved.

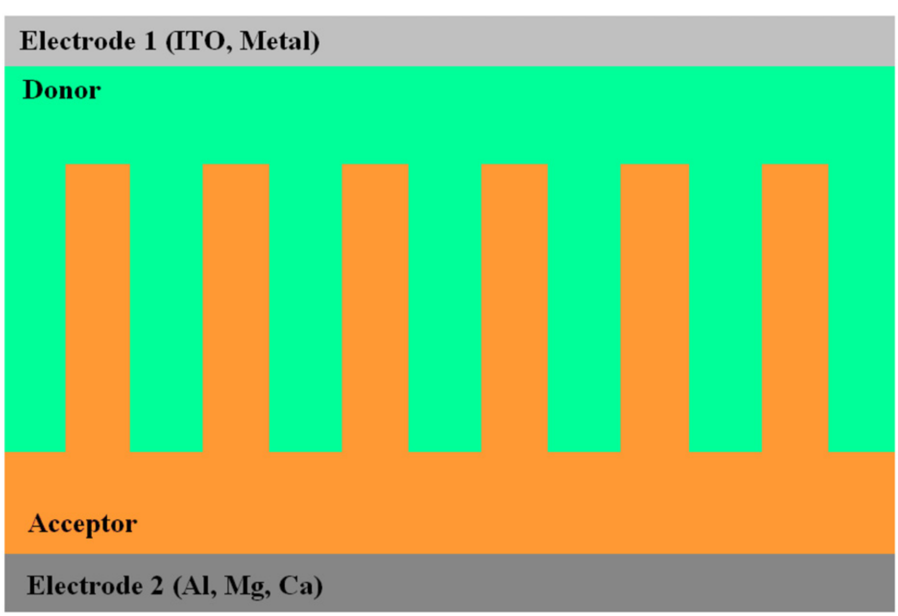


Fig. 8. The schematic of an ideal OHJ, in which all absorbed photons are in the vicinity of a D–A interface and can contribute to photocurrent generation.

Kymakis et al. [50]. have studied an ordered array of D–A interface containing a blend of single-wall carbon nanotubes (SWNTs) as the acceptor and soluble polythiophenes (P3OT) as the donor. The V_{oc} of the devices has reached 0.75 V, which is higher than expected. Their research have proposed that such photovoltaic response is caused by the internal polymer/nanotube junctions within the polymer matrix. Due to a photoinduced electron transfer from the polymer to the nanotube, the polymer/nanotube junctions have enhanced both the charge separation and the charge collection. Although the transport of the electrons and holes toward electrodes is uninterrupted once the excitons are disassociated, yet the nanotubes do not support photogeneration. The photocurrent of such devices is relatively low due to the incomplete phase separation and the limited light absorption caused by the mismatch between the polymer's spectral response and the solar spectrum. This is a typical case that demonstrates the different phases of photocurrent generation are interconnected. Improving a single phase not necessarily leads to the overall cell performance enhancement as one might expect.

3. Other potential materials and structures

Efficient combinations of two polymerization reactions have been noted to have desirable photovoltaic qualities. These qualities include crystallinity, light absorption, microphase separation, photoluminescence quenching, and the presence of D–A heterojunctions [51].

Block copolymers (BCPs) are produced by joining two or more chemically distinct polymer blocks. Each of these blocks is a linear series of identical monomers that may be thermodynamically incompatible. Meyers et al. [52] have presented their modeling and calculation results to determine the electronic properties and the geometric structure evolution as a function of unit cell content in the regular BCPs. They have foreseen the potential of BCPs for solar cell devices. BCPs can have periodic, adjustable nanostructures [53] and can be tuned for a wide range of applications. An ideal BCP for OPVCs is synthesized with a p-type block and an n-type block. The main issue for the polymer–polymer based solar cells technology resides in the synthesis of conducting acceptor polymers that have the property similar to that of fullerenes.

Halls et al. [24] have shown that the interpenetrating network formed from a phase-segregated mixture of two semiconducting polymers provides spatially distributed interfaces needed for efficient charge photo generation. The same device also provides the means for separately collecting the electrons and holes. Yu and Heeger [54] have described a phaseseparated polymer blend with MEHPPV as donor and CNPPV as acceptor to show that the photosensitivity of OPVCs can be enhanced by blending donor and acceptor polymers to optimize photo-induced charge separation. Zhang et al. [55] have synthesize the D–A diblock copolymers with regioregular poly(3-hexylthiophene) (*rr*P3HT, a donor) and poly(perylene diimide acrylate) (PPDA, an acceptor). They have used the polymers to produce a solar cell that have shown a 0.49% power conversion efficiency. Such performance is typical as the efficiencies of BCP-based OPVCs are generally below 0.5%.

Liquid crystals (LC) have advantageous electronic properties and been researched as a new generation of OPVC material. Liquid characteristic of LCs enable the self-repair of its structural defects. Discotic (disk-like) liquid crystals have an increasingly significant role in the field of organic molecular electronics [56–58]. A highly ordered columnar (stacked) phase of discotic organic molecules exhibit high mobility for photo-induced charge carriers [59]. Conjugated LCs have potentials in controlling the order in the bulk and at interfaces of OPVCs from the molecular to the macroscopic scale. The low molecular weight of conjugated LCs allows defect-free chemical structures and high purity levels. Large single domains of LCs can be achieved via thermal annealing [60,61]. Molecules inside these large domains can be oriented via a variety of mechanisms such as aligning surface layer [62,63] applying polarized irradiation [64], and tuning the concentration or the temperature [65,66].

4. Issues and recent highlights

4.1. Cell stability

In spite of the high development potential of OPVCs, considerable improvement of their stability under operational conditions needs to be achieved. Device durability that involves chemical stability and degradation of polymers has always been an important issue for OPVCs. Studies [67–72] have indicated that the degradation mechanisms in OPVCs include reaction with O_2, H_2O, and the electrode materials. Therefore, to increase the stability of OPVCs requires careful selection of donor, acceptor, electrode, and encapsulation materials.

As for the interface stability issue, aluminum, titanium and silver have been used as the bottom cathode and reflective layer of top-illuminated OPVCs [73–75], These metal-based electrodes showed superior sheet resistance to those of the conventional ITO electrodes.

Studies of unencapsulated OPVC lifetime [76–78] have demonstrated efficiency half life of greater than 1500 h. Potscavage et al. [79] have noted that the shelf lifetime of a pentacene/C_{60} cell encapsulated with an Al_2O_3 film deposited by atomic layer deposition has degraded by 6% over a 6100 h period, compared to a lifetime of < 10 h for an unencapsulated cell.

Barbec [80] has estimated that a cell lifetimes of at least 5 years (about 45,000 h) are necessary for the commercialization of organic solar cells. The research findings below are promising for OPVC to exhibit ultimately sufficient lifetimes that meet Barbec's estimation:

Krebs and Spanggaard [81] have projected, even though for a rather low-performance device, the lifetime of large-area polymerbased bulk HJ devices to be over 10,000 h. Hinsch et al. [82] and Wang et al. [83] have shown very stable dye-sensitized solar cells that have lifetimes in the 5–10 year range. In addition, Kroon et al. [2] have demonstrated the organic LEDs made with small molecular weight semiconductors that have lifetimes of $> 10{,}000$ h.

The commercialization of OPVCs relies greatly upon the understanding of the degradation phenomena such as recrystallization, temperature variations, as well as instabilities against oxidation and reduction. The understanding will lead to the development of new materials, efficient OPVC encapsulation, and the alternative barrier layers which are more resistant to oxygen and water.

4.2. Electrode flexibility and module cost

OPVCs require electrodes with properties that include high transparency, good conductivity and smooth surface. The degree to which a transparent conductor possesses these properties affects the performance of OPVCs greatly.

Due to ITO's high optical transparency, it is widely used as transparent electrodes and substrate in OPVCs. While ITO electrodes present many advantages in the OPVCs fabrication, its limited flexibility makes it less suitable for the substrates that call for better elasticity. The stability between the organic materials and the ITO surface is also less than satisfactory. In addition, indium is a scarce and expensive element that can hurdle the

large-scale OPVC production [84]. On top of these disadvantages, the ITO electrode is fabricated via costly and energy-intensive vacuum-based sputtering [85].

The recently reported alternatives of transparent electrodes that have the potential to resolve the issue of the vacuum-based evaporation with large equipment and operating costs include poly (3,4-ethylenedioxythiophene): poly(styre-nesulfonate) (PEDOT:PSS) with metal grids [86,87], carbon nanotubes [88], graphene [89], and silver nanowires [90–92]. These alternatives can be fabricated via inkjet printing, screen printing, slot-die coating, or other economical processes. Other candidates for ITO-free transparent conductors include semitransparent or patterned metal layers, doped metal oxides, conductive polymers, and metal nanowires. Christopher et al. [93] have conducted a life cycle and cost analysis of several promising ITO-free transparent conductors and demonstrated that replacing ITO with an alternative transparent conductor tends to reduce energy pay-back time and OPVC module cost.

4.3. Production and Niches

The conversion efficiency and operational stability for OPVCs is approaching the key 10–10 targets (10% efficiency and 10 years of stability) through lab researches and early commercial efforts. Before the applications of OPVCs reach their full potential, there are still challenges stand between the lab and the realistic industrial processes. Søndergaard et al. [94] have reviewed some roll-to-roll processing (a technique to create OPVCs on a roll of flexible plastic) required to bring the 10–10 targets into reality. The review covers a variety of quick methods that involve low cost and low environmental impact and highlight some new targets related to processing speed, materials, and environmental impact.



Fig. 9. An a-Si photovoltaic module with laser inscribed image pattern (courtesy of Dr. Shui-Yang Lien, Solar Energy Center, MingDao University).

The integration of OPVCs' with clothing for powering personal electronic devices is forthcoming. Kylberg et al. [95] have demonstrated a flexible and transparent electrode mesh based on a fabric with metal wires and polymer fibers woven together. Lipomi et al. have introduced a stretchable organic solar cell fabricated via spin-coating the transparent electrode and active layer on a pre-strained elastomeric membrane. Their experiment have shown that the device have presented similar photovoltaic properties, stretched and unstretched [96]. This development can certainly facilitate a highly portable photovoltaic fabric solar tent integrated with interior LED lighting, underfloor heating, and electronic devices charger.

The vehicle as well as building-integrated photovoltaic technology has been a promising area for thin film solar cells. Translucent amorphous silicon (a-Si) photovoltaic module has expanded the range of building-integrated photovoltaic applications to include sunroofs, skylights, and windows [97]. In addition to efficiency enhancement, researchers have been focusing on improving photovoltaic module appearance to attract market shares. Lien et al. [98] have developed an image-patterned translucent a-Si photovoltaic module. They successfully inscribe an 1100 by 1400 mm^2 image-patterned on a translucent photovoltaic module (Fig. 9). The module exhibits a stable maximum power output of 92.5 W, compared to the 115.2 W output before the inscription. Other than gray-scaled logos, these researchers have demonstrated capabilities to display colored photos on the module via laser inscription. This application is appealing in both the energy generation and the aesthetic aspects. While the amorphous silicon is not exactly an organic material, it is not far fetched reality to apply laser inscription technique to OPVCs and create similar aesthetic effects that appeal to the industry and consumer markets.

4.4. Record of efficiencies

The photovoltaic technologies are generally divided into five categories as shown in Table 2. The silicon wafer-based photovoltaic

Table 2
Best research-cell efficiencies as of 2012/5, compiled from National Renewable Energy Laboratory's chart of best research-cell efficiencies [103].

Category	Type	Efficiency (%)	Research organization
Multi-junction concentrators (2-terminal, monolithic)	Three-junction (concentrator)	43.50	Solar Junction
	Three-junction (non-concentrator)	35.80	Sharp
	Two-junction (2-terminal, monolithic)	32.60	FhG-ISE
Single-Junction GaAs	Concentrator	29.10	FhG-ISE
	Thin film crystal	28.80	Alta Devices
	Single crystal	26.40	FhG-ISE
Crystalline Si cells	Single crystal	27.60	Alta Devices
	Silicon Heterostructures (HIT)	23.00	Sanyo
	Multicrystalline	20.40	FhG-ISE
	Thick Si film	16.00	Sharp
Thin-film technologies	Cu(In,Ga)Se2	20.30	ZSW
	CdTe	17.30	First Solar
	Nano-, micro-, poly-Si	17.20	Univ. Stuttgart
	Multi-junction polycrystalline	15.00	NREL
	Amorphous Si:H (stabilized)	12.50	United Solar
Emerging photovoltaic	Dye-sensitized cells	11.80	NTU/Singapore
	Organic cells (various technologies)	10.16	Sumitomo Chemical
	Inorganic cells	10.00	IBM
	Organic tandem cells	8.60	UCLA
	Quantum dot cells	5.10	Univ. of Toronto

cells that include the single crystal, the multi-crystalline, and the hetero-structure (i. e., mixed single crystal/amorphous) cells belong to the first generation. The first generation technology is the current mainstream, which has over 80% of the market share. The record conversion efficiency of multi-crystalline photovoltaic cell is 20.4%, while the single crystal silicon can reach a high of 26.4%.

The single junction, the multi-junction, and the thin film solar cells belong to the second generation. The thin-film photovoltaic cells includes the II–VI family (e.g., CdTe), the I–II–VI family (e.g., $CuInSe_2$), the amorphous silicon, and the microcrystalline silicon cells. The record conversion efficiency of amorphous silicon cell is 12.5%, while the high efficiency of CdTe and $CuInSe_2$ are 17.3% and 20.3%, respectively. The microcrystalline silicon has seen a breakthrough recently and has reached an efficiency close to that of CdTe.

The third-generation photovoltaic cell technology is still in the early development stage. Common third-generation photovoltaic cells include but not limited to organic dye, quantum well, nanotube, multi-layer (or tandem) cells, non-semiconductor technologies (e.g., OPVCs), and intermediate band solar cell [99–101]. The cost and benefit ratio of the third generation technology is still too high to be competitive with their previous generation counterpart. A research [102] that aims to increase the cell efficiency to over 10% via existing techniques such as screen printing and continuous roll-to-roll processes is underway. The researchers involved intend to use a tandem architecture that stacks OPVCs on top of each other for better sunlight interception. Such combination of multiple cells involves complementary levels of light absorption and thus helps to achieve better efficiency.

The efficiencies shown in Table 2 are the laboratory test results. The actual conversion efficiencies in the final mass production should be less compared to the lab performance. Nevertheless, the recent increases in efficiency along with the growing research community in OPVCs indicate that commercially viable efficiency of greater than 10% is feasible. A multidisciplinary cooperation among physics, chemistry, engineering, and material science communities will for sure speed up the progress.

5. Conclusion and other discussion

This paper briefly introduces the device physics underlying OPVCs of D–A interfaces, then discusses important factors include the exciton diffusion length as well as charge transport, separation, and collection.

The power conversion efficiency of OPVCs has increased steadily after the introduction of the donor–acceptor heterojunction that functions as a dissociation site for the strongly bound photogenerated excitons. Further progress has been realized in polymer devices through the use of blends of the donor and acceptor materials. Phase separation during spin-coating leads to a BHJ, an interpenetrating network of the donor and acceptor materials. BHJ greatly expand the area of the interface between donor and acceptor, which leads to a great production of separated charges. But the random nature of the phase interface tends to get in the way of the charges heading for the electrodes.

To improve the charge separation processes and the transport of the free charge to the electrodes, efforts in acquiring bulk-ordered interface of donor and acceptor materials are needed. One promising approach is to explore the structure of the **ordered heterojunction** (OHJ), which provide better D–A materials positioning and thus better quantum efficiency. Other promising ways to obtain fine cell bulk architectures are to use liquid crystal semiconductor molecules and to study phase separation strategies between these base components.

Improving the V_{oc} and the short circuit I_{sc} should be deemed the central approach to enhance the power conversion efficiency. Finding new and improved materials and identifying high performance donor–acceptor pairs is important to simultaneously optimize V_{oc} and I_{sc}. In addition, careful architectures such as optical design that ensure the active layers are under maximum incident light intensity will also assure the continued efficiency improvement.

Ever since the discovery of organic solar cells, much progress has been made via the collaboration between synthetic organic chemists and physicists in academia and industry. There is no doubt that rooms for improvement still exist. The challenge of OPVCs' commercialization is in the development of large-area modules with long operational lifetimes, high production yields, low production costs, and high efficiency.

In comparison with inorganic photovoltaic devices, difficulties associated with OPVCs include their low QE due largely to the large band gap of organic materials. Re-crystallization, temperature variations, and instabilities against oxidation and reduction also lead to device deterioration and performance degradation over time. These factors arise to different extents for devices with different compositions, and are where active research should be worthwhile.

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